Electrically tunable window device

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A device for controlling the transmittance of light over large areas, such as windows, is described. It is based on electrostatically-induced surface deformation of soft dielectric elastomer sheets produced when a voltage is applied between two networks of electrically-conducting nanowires on either side of the elastomer. Variations in the surface curvature produced by the applied voltage refract light, decreasing the optical transmittance at all wavelengths. As the device relies on changes in the geometric propagation of light rather than on chemical changes, it is color neutral.

In contrast to the large number of devices that have been developed for modulating laser beams, there are few that can be used to modulate the optical transmittance over large areas, such as windows in buildings and transportation vehicles. The best known are electrically-controlled polymer-dispersed liquid crystal films (PDLC) and electrochromic devices [1]. PDLC films consist of droplets of liquid crystals suspended in a polymer matrix which is sandwiched between two electroded polymer films. In the absence of electric field, the crystals within the droplets are randomly oriented which scatter incoming light. When electric field is applied to the electrode, the crystals are aligned to the direction of the field reducing the scatter and resulting in transparency [2,3]. Such control of particle alignments under an electric field is generalized in suspended particle devices that use anisotropic particles such as rods suspended in a fluid layer [4–6]. Electrochromic devices consist of layers of electrodes and active materials sandwiched in between two glass panes. The composition of the active materials includes a host transition metal oxide and mobile ionic species, such as tungsten oxide and hydrogen ions, respectively. When a voltage is applied, current flows resulting in an electrochemical reaction which changes the oxidation states of the active materials. Since the oxidation state of the active materials have different optical properties, for instance, opacity, the electrical current consequently changes the optical transmittance from clear to dark or vice versa. There is usually a corresponding color change, a blueish tint for the tungsten oxide windows. In a variant of these devices, using transition-metal hydrides, the window can be switched from a clear to a reflective state, rather than being absorbing [1].

In this report we describe the use of random networks of nanowires to create local surface deformations of a soft elastomer film which, in turn, can be used to control light transmission through the elastomer. The underlying concept is similar to the principle of operation of dielectric elastomer actuators. In these, a voltage is applied across the thickness of a dielectric and the Coulombic attraction between the opposing charges on flat electrodes leads to a spatially uniform Maxwell stress that compresses the dielectric. The magnitude of this stress is $2 = {}_{r} {}_{o} E^2$, where E is the electric field and ${}_{r}$ is the relative permittivity of the dielectric. In most dielectrics, the resulting deformation strain are very small (ppb to few ppm) since their elastic moduli are high, typically ~100 GPa for oxides in capacitors and piezoelectrics. However, the elastic moduli of elastomers are commonly 10-1000 kPa and so the displacements produced are correspondingly orders of magnitude greater. When a percolative electrical network of conducting nanowires is used in place of a flat, continuous plate electrode there is both a macroscopic compression of the elastomer arising from the average charge distribution over the conducting nanowire network together with spatially varying local displacements associated with electrostatic force on individual nanowires. As will be shown, the resulting voltage-induced surface displacements alter the optical transmittance and can be used as a voltage controlled light modulator.

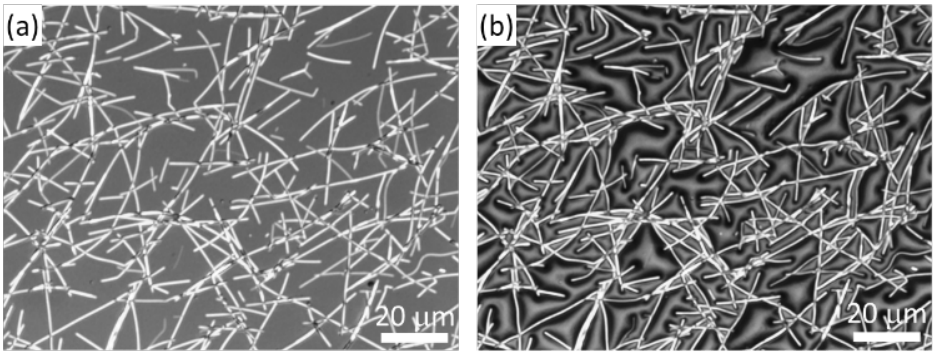

Fig. 1. Bright field optical microscope images illustrating the random arrangement of silver nanowires (90nm ave. diameter, 20-60 m length, SLW-NW-90, Blue Nano, Charlotte, NC) dispersed on the surface of an elastomer sheet. (b) The same area and imaging conditions when a voltage is applied with respect to a flat electrode underneath. The nominal electric field is 110 V/ m. The variations in contrast in the vicinity of the nanowires are due to variations in local curvature associated with the nanowires being displaced downwards relative to the average surface. Bulging of the surface in between the nanowires is most pronounced where the fibers are well separated.

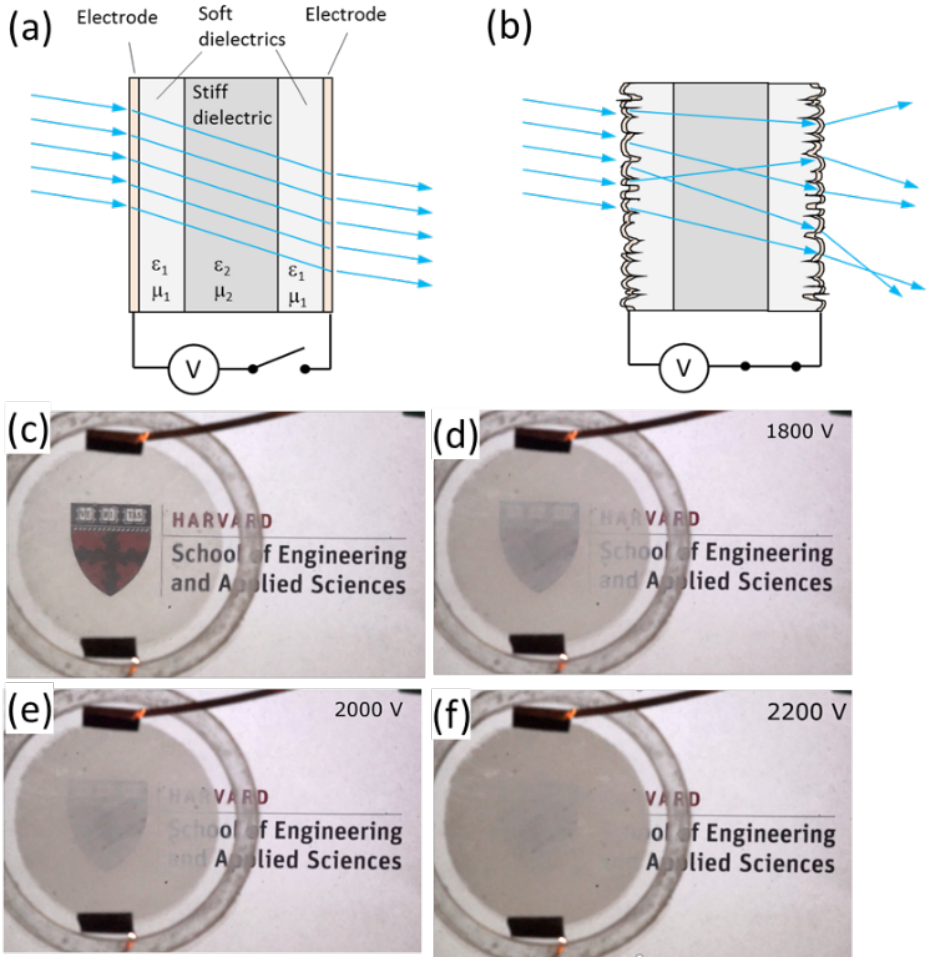

Fig. 2. (a) Schematic cross-section diagram of the two-layer device consisting of two layers of silver nanowires, two soft elastomer dielectrics (polyacrylate film) separated by a stiff dielectric (Mylar film). In the absence of an electric field, the surfaces are relatively smooth and light passes through without being scattered or refracted. (b) When connected to a high voltage source, the nanowires locally compress the elastomer deforming its surface. Since the nanowires are randomly oriented, the resulting deformation diffuses light passing through the device. (c) to (f) Changes of opacity at the indicated actuation voltage from 0 to 2.2 kV, demonstrating control over the in-line transmittance using electrical potential. The logo

and text are located 15 cm behind the circular film. The black rectangles are electrical contacts to the two sides of nanowire electrodes. The real-time video switching from 0 to 2200 V is provided in the Visualization 1 in the Supporting Information.

The simplest device structure consists of a thin nanowire mat, such as a network of silver nanowires, on a uniform thickness elastomer film attached to a transparent, stiff substrate, such as an ITO coated glass sheet. The substrate is not only transparent but also is much stiffer than the elastomer. Consequently, the substrate constrains the lateral expansion of the elastomer film when the voltage is applied ensuring that the Coulombic forces produce displacements primarily in the thickness direction. As the nanowires are randomly distributed over the surface of the elastomer, the vertical displacements also vary with position, altering the surface morphology. This is illustrated by comparing the bright field microscope images shown in Fig. 1(a) before and 1(b) with a voltage applied. The individual nanowires are visible because of their high optical reflectance. With no voltage applied, the elastomer appears uniformly grey but when a voltage is applied, there are variations in contrast in the optical image, mostly in the immediate vicinity of the nanowires.

An alternative form of the window device is shown schematically in Fig. 2 where light has to pass through two elastomer surfaces each with a nanowire electrode. In this structure, the continuous ITO electrode on glass is replaced with a second nanowire network on the opposite side of an intervening transparent sheet such as a stiff polymer or thin glass sheet. To create this laminated structure two thin polyacrylate elastomer films (3M VHB F9460PC, nominal thickness 50 m) were biaxially pre-stretched to 300% linear strain, resulting in thickness of 3.1 m and then laminated on both sides of a Mylar (polyethylene terephthalate) sheet (13 m thickness). This eliminates the need for the continuous ITO electrode. Light passing through this device structure is incoherently refracted twice, once by the front deformable surface and then again by the back deformable surface.

Dramatic changes in the light transmittance upon application of an electric field are shown in Fig. 2(c) to 2(f). These images, recorded at successively higher applied voltages, are of a logo and letters placed 15 cm behind a device mounted on a circular ring. Initially visible when no voltage is applied, they become progressively less visible as the voltage was increased to 2.2 kV at 3Hz. (The reason for using an alternating voltage is discussed in a later paragraph). The transition from transparent to nearly opaque occurs in less than 1 second and is reversible as shown in the Visualization 1 in the Supporting Information.

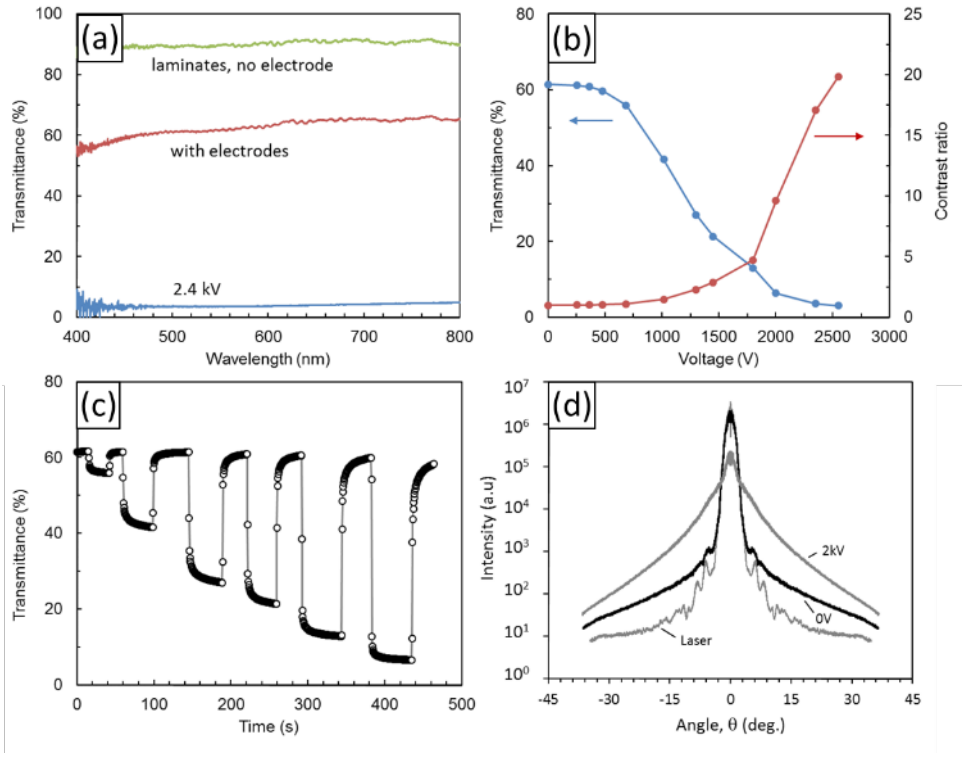

Fig. 3.(a) The in-line spectral transmittance of the double layer device with nanowire electrodes. A significant decrease in the in-line transmittance is observed at all wavelengths with the applications of 2.4 kV. (b) The optical transmittance at a wavelength of 550 nm and corresponding contrast ratio (T_{max}/T) as a function of electrical voltage. (The lines are guides to the eye). (c) Response time of the device upon application of increasing actuation voltage from 700 V to 2000 V. Sampling

period is 0.5 s. (d) Intensity profile of the transmitted light as a function of angle for the indicated applied voltages. This profile was measured by shining He-Ne laser (632 nm, 1 mm beam diameter) normal to the device and by recording the spread of exit beam using a 2D CMOS sensor (15.6x23.5mm, model NEX-3N, Sony Corp.) placed on a translation stage, at a distance of 22mm away from the device.

The optical transmittance data is shown in Fig. 3(a). Without the nanowire electrodes, the three dielectric layers have a combined in-line transmittance of 90%, and most of the light lost is attributed to the surface reflectance at the two interfaces between the elastomer film (polyacrylate, refractive index 1.48-1.50 at 550 nm) and the air. Additional losses may be attributed to several factors including interface losses due to the slight difference in the refractive index between the polyacrylate and Mylar (n = 1.65, at 550 nm) [7,8] and slight light absorption by the polyacrylate. The addition of two layers of silver nanowire electrodes having a density, in this particular case, of 78 mg/m^2, decreases the transmittance to 62%. The decrease is mainly caused by scattering from the metal nanowires, rather than any optical absorption. In this particular device, the in-line transmittance drops to 8% at a voltage of 2.4 kV. The transmission is relatively flat across the visible wavelength, indicating that the laminate is color neutral in contrast to the "blueish" tint normally seen in many electrochromic devices. The transmittance can be tuned continuously between the maximum and minimum transmittance values by controlling the actuation voltage, as shown in Fig. 3(b). The transmittance curve as a function of voltage has a non-linear shape, in particular near the low and high voltages, but is approximately linear between these two extremes. The nonlinearity at the low end limits is a result of the quadratic dependence of Maxwell force on the electric field (equation 1) whereas at the high limit the non-linearity is caused by approaching a saturation in the amount of light that can be scattered. The transmittance response as the voltage is increased to successively larger values and turned off in between is shown in Fig. 3(c). At each change in voltage, there is a rapid change (~ 1 s) in transmittance of about 90% followed by a slower change. Concurrently, as the applied voltage is increased, the transmitted beam broadens. An example, recorded at a wavelength of 632 nm, using a 2D CMOS detector is shown in Fig. 3(d).

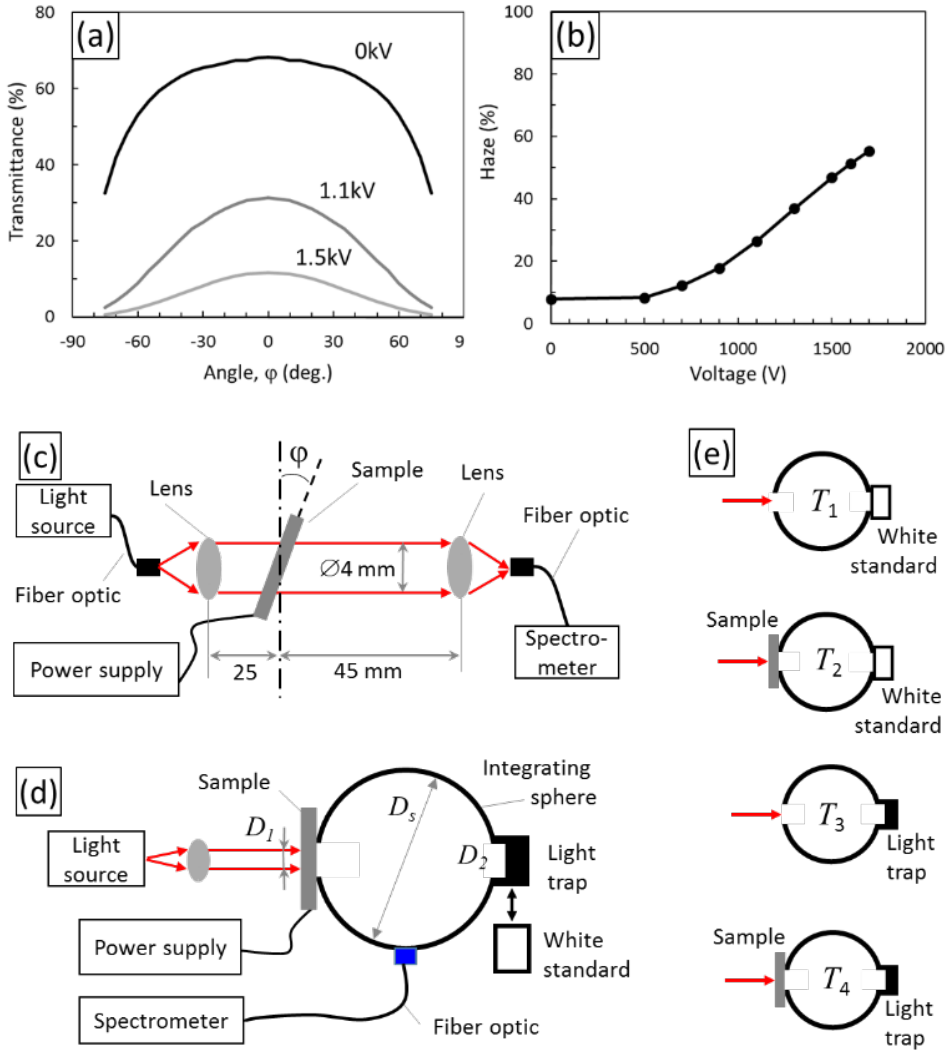

Fig. 4. (a) The in-line transmittance as a function of the incident illumination angle at the indicated actuation voltages. (b) The haze as a function of actuation voltage. (The lines are guides to the eye). (c) Schematic of the in-line optical transmittance as a function of illumination angle, . (d)Schematic of the total transmission and haze measurement. D_1 = 4 mm, D_2 = 7.9 mm, D_s = 38.1 mm. The haze was measured following the ASTM standard[12] using an integrating sphere (Model RSA-FO-150, Labsphere Inc). and a reference white standard (Spectralon SRS-99, Labsphere Inc). The standard specifies that a specular transmission has maximum spread of 2.5 and anything larger is considered to be diffusively scattered. Because of the size of our collimator, we used a slightly different spread angle of 2.9 . (e) Schematic of the integrating-sphere measurements used to determine the total transmission, $T_t = T_2/T_1$, the diffused transmission, $T_d = [T_4 - T_3 (T_2/T_1)]/T_1$, and the haze = $(T_4/T_2 - T_3/T_1)$ x 100%.

The effect of viewing angle is shown in Fig. 4. The in-line transmittance as a function of the illumination angle is shown in Fig. 4(a). Without any voltage applied, the direct transmittance is relatively flat between 45 , and diminishes quickly above about 50 . This is close to the Brewster angle, 56 , calculated a flat interface between air and polyacrylate. (The Brewster angle is the angle at which the surface becomes highly reflected to the incident light that has electric field vector perpendicular to the surface. At this angle, half of the intensity of the incident light (assuming non-polarized) is reflected causing a rapid decrease in the transmitted intensity). The intensity roll-off is less pronounced than for a smooth elastomer without any nanowires, indicating that the nanowires produce the equivalent of an optical roughness. When a voltage is applied, the transmittance at normal angle decreases and its variation with angle increases. This effect is typically caused by rough surfaces that increase the diffuse scattering, consistent with the smoother roll-off in transmittance with viewing angle at the higher voltages in Fig. 4(a). It is also consistent with the broadening at a single wavelength shown in Fig. 3(d). The haze, defined by $I_{scatter}/I_{total}$ x 100%, where I_{total} is the total intensity of incoming light and $I_{scatter}$ is the integrated intensity of spread beam surrounding the original transmitted beam, as a function of voltage as shown in Fig. 4(b). In the absence of any voltage, the device has an intrinsic haze of 8%. This value depends on the density of the silver nanowire mats. Note, that because of technical difficulties, the maximum voltage used for haze measurement was limited to 1700V. It is anticipated that the haze will increase with still higher voltages".

As mentioned earlier, the graphs presented as a function of voltage was recorded under AC conditions. This was because it was observed that under a constant DC voltage, the light transmission decreased rapidly in less than 0.5 second followed by a slow increase reverting toward its original transmittance. This behavior is shown in Fig. 5(a). Under AC conditions, this phenomenon was not observed. The drift suggests that there is a change of the electric field induced surface morphology with time. Two explanations are possible, a viscoelastic relaxation of the elastomer and a charge re-distribution. To learn if the intrinsic viscosity of the elastomer was responsible for the decay, a comparison was made between two devices, one made with the polyacrylate and the other with a silicone elastomer, an elastomer that is known to exhibit much less viscoelasticity. The low viscoelasticity of the silicone is evident from the faster response time compare to polyacrylate, which can be seen from the higher curvature after the polarity of the power supply is reversed (see arrow 'a' in Fig. 5(b)). However, after prolonged times, as indicated by arrows 'b' in Fig. 5(b), both curves become relatively linear with similar slope. This is a strong indication that the same process governs the observed response in either material. Based on this comparison, it was concluded that viscoelastic relaxation is not responsible for the observed drift.

The other mechanism that might be responsible for the transmittance drift is migration of charge from the nanowire electrodes spreading out over the surface of the elastomer. The effect of charge re-distribution would be to decrease the local electric field on the nanowires and consequently also the electrostatic force on the nanowires locally deforming the elastomer. In turn, the effective roughness of the elastomer would decrease, leading to an increase in the in-line transmittance. In the limit, the charge would migrate until it is uniformly distributed over the surface and the morphology would be the same as in the absence of the applied voltage. Based on images such as Fig. 1(b) it is likely that the charge re-distribution would be most pronounced at the ends of individual nanowires as these have a very small radius of curvature. This would be the surface analog of charge spraying from a pointed conductor as originally observed by Röntgen [9] over a hundred years ago and employed in the Xerography process. More recently, charge spraying from a high-voltage needle has been used to spray charges to actuate dielectric elastomers without physical contact [10].

To limit the effects of charge migration, the voltage was reversed periodically so that the net voltage gradients driving surface charge migration would be zero. The effect of increasing the frequency of the voltage reversal on the in-line transmittance is shown in in Fig. 5(c). As indicated the drift decreases with increasing frequency and is almost completely suppressed at 2 Hz and above. Therefore, we used a square wave power source with frequency of 3 Hz to ensure stable optical transmittance for analysis of the optical performance, such as for the time-evolution data shown in Fig. 3(c). Using AC power rather than DC effectively doubles the response time to a change in the DC value but is still less than a second. The slower response time is attributed to the intrinsic viscoelasticity of the polyacrylate elastomer. Nevertheless, the overall response time is still significantly faster than that reported for electrochromic devices.

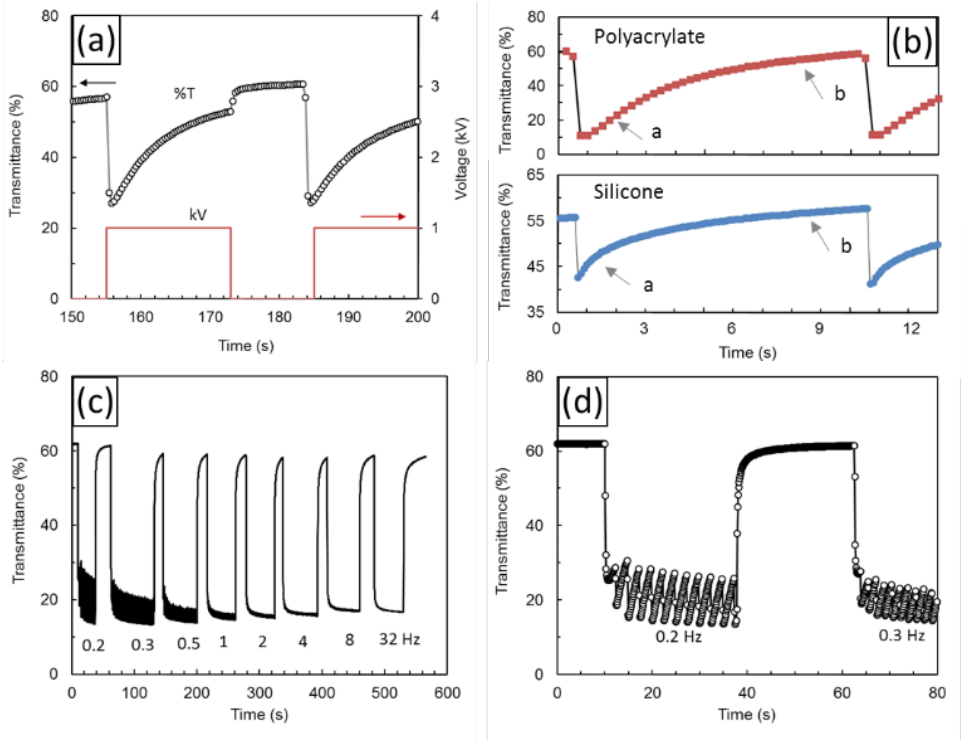

Fig. 5. (a) Optical transmittance response to a square DC voltage pulse. The sampling period between consecutive data points is 0.3s. There is a fast (< 0.5 s) initial decrease in transmittance followed by a slower increase in the transmittance. (b) The transient response of two different elastomers, a polyacrylate (VHB) and a silicone elastomer, are similar suggesting that the response is not limited by a viscoelastic mechanical response of the materials themselves. In these measurements, the polarity of the voltage source was initially reversed at t = 1s and then again after t = 10 s. (c) The dynamic response at different AC voltage frequencies. At switching frequencies of ~ 2 Hz and above, the drift is significantly suppressed. (d) Expanded region of figure (c) indicates saw-tooth profile that corresponds to the reverses in the polarity of the actuation voltage. Sampling period is 0.1s.

There are several intrinsic advantages of the light modulation device described in this work. These include the scalability to much larger areas, the suitability for roll-to-roll manufacture using commercially available materials, notably elastomers and Mylar, as well as the intrinsic light-weight and flexibility of the materials. It is also possible that with some design modification of the laminate structure, the device can be retrofitted to existing windows. It is likely that the current materials can be further optimized in several aspects including increasing the transparency of the elastomer, decreasing the actuation voltage using thinner and softer elastomer, optimizing the density of nanowires for maximum light scattering characteristics, increasing the conductivity of the nanowire network using post processing such as plasmonic welding and the incorporation of SWNT. Although the materials in the device do not absorb in the visible spectrum, it may nevertheless be possible to control heating from solar radiation in the infra-red.

The use of a stiff dielectric inner layer is also important, irrespective of whether it is Mylar or ITO coated glass. Firstly, it can provide support for the thin elastomer films as well as the forces used to stretch the soft elastomer dielectric to decrease its thickness. The main purpose of pre-stretching is to decrease the thickness of the dielectric so as to reduce the actuation voltage. With total thickness of 19 m , actuation voltages of 1 to 2.5 kV produces significant deformation which, as demonstrated above, is sufficient to reduce the in-line optical transmittance by more than 90%. The second reason for having a stiff intervening dielectric is to limit premature electrical breakdown due to electromechanical instability typically found for soft dielectrics [11]. Finally, although similar tunability in optical transmittance can be expected to occur using a regular geometrical electrode mesh, the periodicity of the mesh would likely lead to periodic variations in the transmitted beam. The randomness of the nanowire mat avoids any such preferred directionality in the transmitted light.

In conclusion, we have shown that it is possible to tune the in-line transparency of a transparent window by electrically modifying the surface morphology of a thin elastomer film. The underlying mechanism is the spatially non-uniform deformation produced in the elastomer surface when a voltage is applied to a percolative network of randomly oriented nanowires spread over the elastomer with a counter electrode underneath. The Coulombic attraction between the individual nanowires and the counter-electrode locally deforms the elastomer producing a surface roughness which, in turn, refract incident light. The window devices operate under alternating voltage with a response time of the order of 1 second. The devices made using polymer and elastomer sheets are very lightweight (~25 g/m^2) and flexible, making it easy for transportation and retrofitting into existing windows. Alternative devices can be fabricated with ITO coated glass as the stiff

dielectric. It is anticipated that there will be several practical applications of the optical effects include tunable privacy windows, smart glass, projector screen, displays, and camouflage.

Acknowledgements. This work was supported by the National Science Foundation through grant CMMI-1333835 and in part by the MRSEC program of the National Science Foundation under award number DMR 14-20570.

REFERENCES

1. C. G. Granqvist, "Electrochromics for smart windows: Oxide-based thin films and devices," *Thin Solid Films* **564**, 1–38, Elsevier B.V. (2014) [doi:10.1016/j.tsf.2014.02.002].
2. D. K. Yang, L. C. Chien, and J. W. Doane, "Cholesteric liquid crystal/polymer dispersion for haze-free light shutters," *Appl. Phys. Lett.* **60**(25), 3102–3104 (1992).
3. D. Cupelli et al., "Electrically switchable chromogenic materials for external glazing," *Sol. Energy Mater. Sol. Cells* **93**(3), 329–333 (2009) [doi:10.1016/j.solmat.2008.11.010].
4. G. Beni, H. G. Craighead, and S. Hackwood, "Anisotropic suspension display," *Appl. Phys. Lett.* **39**(3), 195 (1981) [doi:10.1063/1.92700].
5. B. Yu, E. Kim, and Y. Lee, "Developments in Suspended Particle Devices (SPD)," *SPIE Proc.* **3138**, 217–225 (1997).
6. R. Vergaz et al., "Modelling and electro-optical testing of suspended particle devices," *Sol. Energy Mater. Sol. Cells* **92**(11), 1483–1487 (2008) [doi:10.1016/j.solmat.2008.06.018].
7. J. F. Elman et al., "Characterization of biaxially-stretched plastic films by generalized ellipsometry," *Thin Solid Films* **313-314**, 814–818 (1998) [doi:10.1016/S0040-6090(97)01001-8].
8. S. N. Kasarova et al., "Analysis of the dispersion of optical plastic materials," *Opt. Mater. (Amst).* **29**(11), 1481–1490 (2007) [doi:10.1016/j.optmat.2006.07.010].
9. W. C. Röntgen, "Ueber die durch Electricität bewirkten Form- und Volumenänderungen von dielectrischen Körpern," *Ann. Phys.* **247**(13), 771–786, WILEY-VCH Verlag (1880).
10. C. Keplinger et al., "Röntgen's electrode-free elastomer actuators without electromechanical pull-in instability," *Proc. Natl. Acad. Sci.* **107**(10), 4505–4510 (2010) [doi:10.1073/pnas.0913461107].
11. X. Zhao and Z. Suo, "Method to analyze electromechanical stability of dielectric elastomers," *Appl. Phys. Lett.* **91**(6), 061921 (2007) [doi:10.1063/1.2768641].
12. ASTM D1003, *Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics* (2003).